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## IV.A.13 Cost Effective, Efficient Materials for Solid Oxide Fuel Cells

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### Objectives

- **Task 1:** Determine the mechanisms used in surface infusion treatments, including CeOx, for improved oxidation resistance.
- **Task 2:** Melt and fabricate 430ss-related alloys with low Si and Al.
- **Task 3:** Evaluate the effect of syngas on 430-related alloys with low Si and Al.

### Accomplishments

- The mechanism of oxidation resistance found by surface treating candidate materials for interconnects and other balance-of-plant applications has been studied. The mechanism, which is the preferential pre-oxidation of the surface of the material, is enhanced by the fact that the rare earth treatment modifies the scale that is formed which, in turn enhances oxidation resistance and slows scale growth. The mechanism of oxidation resistance by rare earth surface infusion, specifically cerium, will be published in peer reviewed journals during the second half of this year.
- A series of experimental alloys with controlled low levels of Si and Al were melted, fabricated and provided for further evaluation. The majority of the material utilized for producing commercial 430ss is from scrap which necessarily contains Si and Al. Methodologies of removing the Si and/or Al during the melting of cheap, low grade scrap have been postulated and may be the focus of future efforts. All experimental alloys have been made available to any interested parties who wish to evaluate the materials for their specific solid oxide fuel cell (SOFC) environment or application.
- Single environment testing for oxidation (cathode side) has been completed on the experimental

low Si/Al 430ss alloys with and without the rare earth surface infusion treatment. The maximum amount of Si tolerable with respect to area specific resistance (ASR) measurements has not yet been determined, however an upper limit has been developed. Single environment testing on the anode side as well as dual environment testing are currently underway.

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### Introduction

Fuel cells are energy conversion devices that generate electricity and heat by electrochemically combining a gaseous fuel and an oxidizing gas via an ion-conducting electrolyte. The chief characteristic of fuel cells is their ability to convert chemical energy to electrical energy without the need for combustion, thereby giving much higher conversion efficiencies than conventional methods, such as steam turbines. Cost remains the final obstacle that must be overcome for fuel cells to realize their full commercial potential. Many of these costs can be attributed to components in the “balance-of-plant.” Advances in solid-state material manufacturing shows promise for making SOFCs applicable in any power application. Cost reduction can be achieved in component fabrication, materials used, and cell and stack designs. However, balance of plant issues also present problems in the commercialization of fuel cell technology. Specifically for SOFCs, air and fuel need to be heated and cooled at some stage of the process. This requires pumps, piping, heat exchangers, etc. in order to deliver useable electrical power. This project explores materials of construction as a means of developing low cost, high temperature components for SOFC systems.

### Approach

The approach to reaching the goals of this project is three fold. First, it has been shown that rare earth infusion of the base material alloys can enhance the oxidation resistance while maintaining favorable electrical characteristics where required. However, a determination of why the rare earth treatment works has not yet been made. Task 1 of this project looks at determining this mechanism with the goal of determining whether the candidate rare earth (cerium) is the best fit for the lowest cost. The second task looks at the silicon and aluminum levels in 430-like stainless steels. It is well known that silicon forms a protective layer on the surface of the alloy in oxidizing environments. However, this protective layer is electrically insulative, an

undesirable characteristic for interconnect applications. This task looks to minimize the silicon levels while maintaining the operational integrity of the alloy. Finally, Task 3 looks at single and dual environment corrosion mechanisms in the experimental alloys, as well as other commercially available alloys, with and without the rare earth treatment, in order to determine the different corrosion characteristics. Moreover, the task looks at determining what, if any, deleterious effects can be seen across a metallic material in the case that there are different (hot) gases flowing on either side of the material.

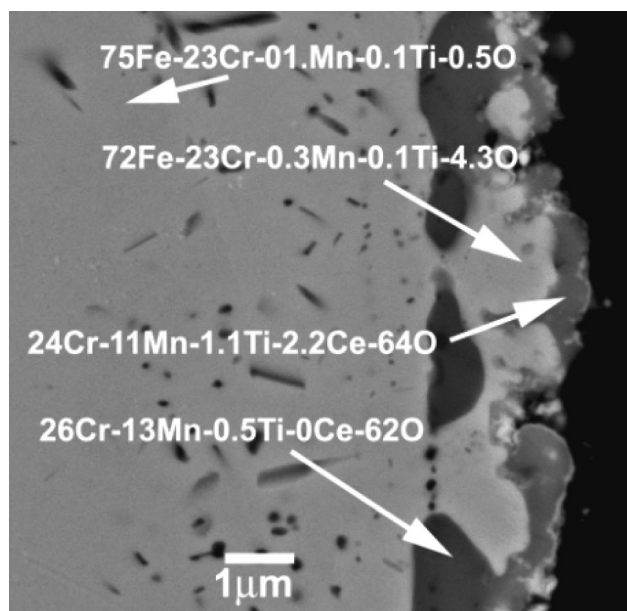
## Results

**Task 1** – Determine the mechanisms used in surface infusion treatments, including CeOx, for improved oxidation resistance.

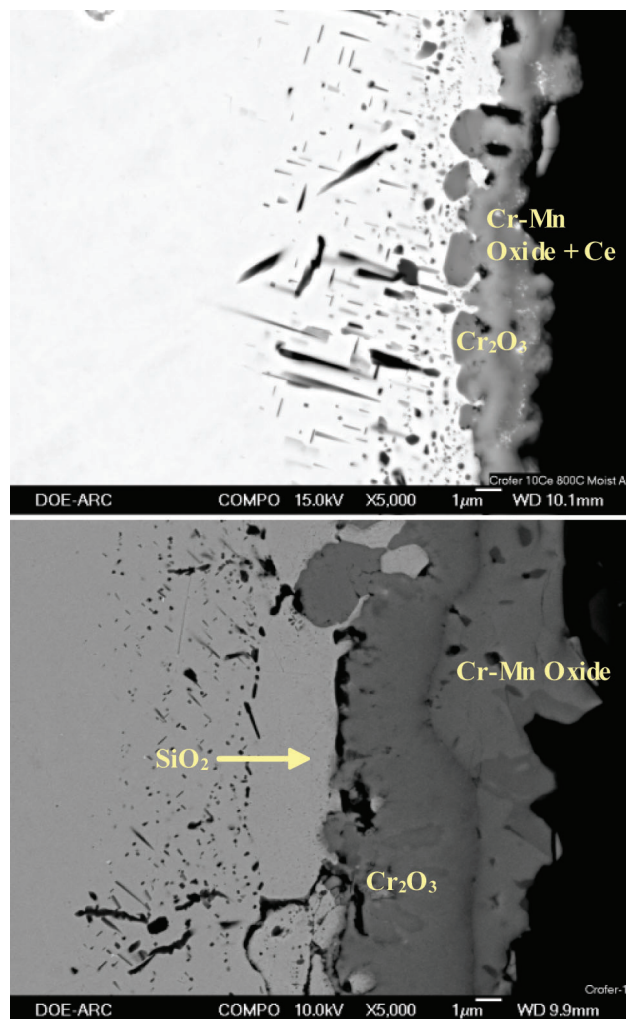
**Progress** – A number of alloys have been treated with the NETL-Albany surface infusion process including the NETL-Albany 430 family of alloys (Task 2) and Crofer 22APU, which is used for baseline studies. After surface treatment,  $\text{CeCrO}_3$ -type and Cr-Mn oxides formed on the surface of the Fe-22Cr-Mn current collectors, as determined by the X-ray diffraction scans obtained from the surface of the sample cross sectioned in Figure 1.  $\text{CeCrO}_3$ -type oxides have been found to form in chromia forming alloys doped with rare earths [1, 2]. The X-ray diffraction results also show that subjecting the alloy to only the thermal portion of the treatment, without the presence of  $\text{CeO}_2$ , does not

result in pre-oxidation. As previously reported, coupons subjected to only the thermal portion of the treatment oxidized in an identical manner as polished samples [3]. Only in the presence of  $\text{CeO}_2$  does pre-oxidation occur during treatment, biasing the surface to form a more slowly growing, and hence, a more protective oxide scale during subsequent exposure.

Examination of the oxide scales through scanning electron microscopy-wavelength dispersive X-ray (SEM-WDX) analysis has shown that the outer Cr-Mn spinel scale contains Ce (Figure 2). The addition of rare earth modifies  $\text{Cr}_2\text{O}_3$  formation, from cation (metal) controlled to (oxygen) anion controlled. This inversion has been found to be accompanied by modification in  $\text{Cr}_2\text{O}_3$  structures from large columnar grains in the undoped scale to small grain structure in the doped scale. Consequently, diffusion of oxygen inward is slowed, resulting in slower scale growth and less internal oxidation.



**FIGURE 1.** Cross section of Crofer 22APU after Ce-surface treatment. Compositions for Cr, Mn, Ti, Fe, Ce are in atomic percent and were determined by WDX analyses in a field emission SEM.

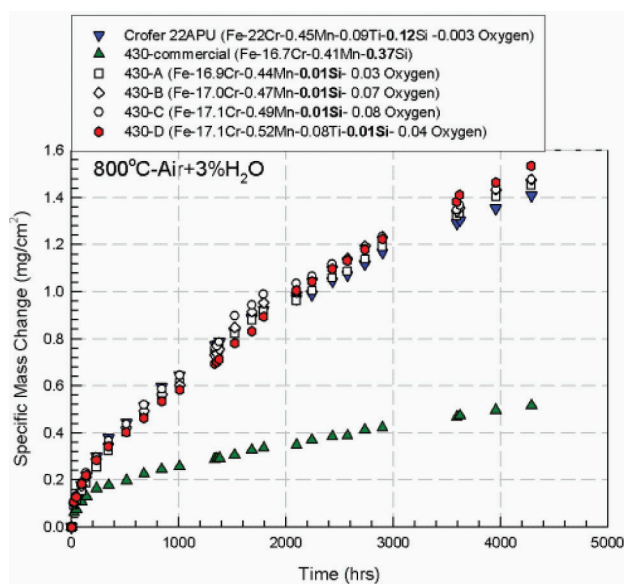


**FIGURE 2.** Comparison of Scale that Formed on: (a) Ce Surface Treated Crofer-22APU and (b) Untreated Crofer 22APU after 2,000 Hours Exposure at 800°C to Moist Air

### A. Oxidation of Ce-treated 430 Alloys

Figure 3 illustrates the influence of Si content on the oxidation behavior (800°C in moist air) of custom Type-430 alloys melted and reduced to sheet at NETL-Albany. In Figure 3, the behavior of 430 is compared with Crofer 22APU. These results clearly demonstrate the effect of high Si content on the oxidation resistance. The commercial 430 alloy, with almost 0.4 wt% Si, has the lowest mass gain during testing, implying it is the most oxidation resistant alloy. However, it should be mentioned that previous testing at NETL-Albany has shown that commercial 430 with high Si levels can spall during oxidation, leading to variability in mass change results and the appearance of superior performance (oxidation resistance). The mass gain of the low-Si 430 alloys is similar in magnitude to Crofer 22APU. It is interesting to note that a trend is emerging that indicates Crofer 22APU is more oxidation resistant, that is, after about 2,500 hours of exposure Crofer 22APU consistently shows a slightly lower mass gain than the low Si 430 alloys. However, this is not surprising since Crofer has a higher Cr content than 430 (22 wt% compared to 17 wt%).

Figure 4 illustrates the effect of the Ce surface treatment on the oxidation behavior on the alloys. It is clear that at 800°C the surface treatment enhances oxidation resistance of all the alloys. The mass gain during oxidation of the low Si-430 alloys has been reduced by a factor of three to four with the Ce treatment, and is equivalent to the commercial high Si 430 alloy. Although not clearly shown on the figure, the Ce-treated commercial 430 alloy had a slightly higher mass gain than the alloy in the untreated condition.



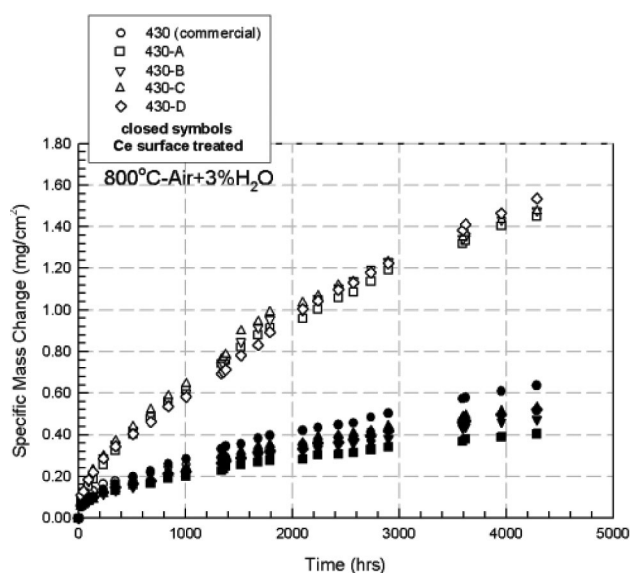
**FIGURE 3.** Comparison of the Oxidation Behavior of Low-Si Type 430 to Commercial Type-430 (high-Si) and Crofer 22APU

However, as mentioned above the apparent superior oxidation resistance of the untreated 430 is due to oxide scale spallation. The Ce treated samples do not spall during oxidation.

Note: These tests are on going and are part of an experiment to assess the long term effectiveness of the Ce-treatment on the behavior of alloys.

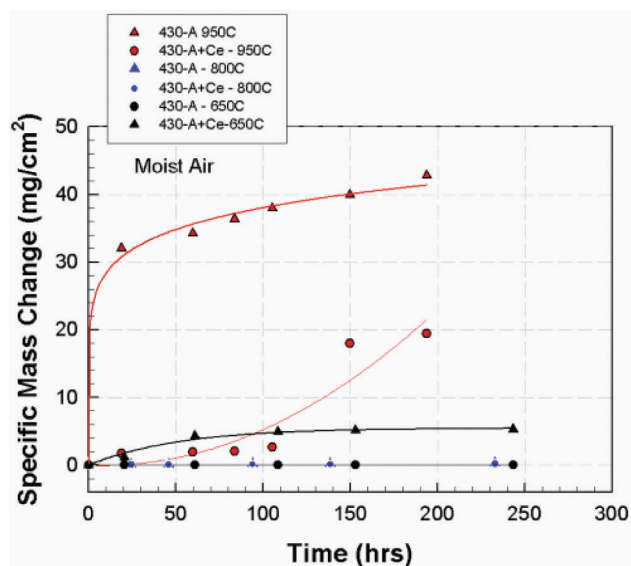
### B. Influence of Temperature on Oxidation Behavior of Ce-treated Alloys

Figure 5 summarizes the effect of temperature on the oxidation behavior for alloy 430-A while Table 1 summarizes the scales that formed on this alloy as a function of test temperature (as determined by X-ray diffraction [XRD]). Of note is that at 950°C, Chromia and Cr-Mn oxide formed on the surface of the Ce-treated alloy, although Fe<sub>2</sub>O<sub>3</sub> was also detected. The formation of Fe<sub>2</sub>O<sub>3</sub> leads to the accelerated behavior displayed by the alloys after a few hundred hours of exposure. Furthermore, it is noteworthy that this alloy is two phase (ferrite plus austenite) at 950°C while it is single phase ferrite below about 875°C. At 800°C, a Cr<sub>2</sub>O<sub>3</sub> scale and Cr-Mn oxide formed on the surface of the alloy in both conditions. Interestingly, at 650°C, only Fe<sub>2</sub>O<sub>3</sub> was detected on the untreated and treated alloys. The base Fe-Cr (bcc) metal phase is the primary phase detected on the surface of the 430-A in the untreated condition. This is not surprising, based on the extremely small weight gain (hence expected thin oxide layer) on this alloy (650°C, 250 hours). Hematite was the major phase detected on the surface of the 430-A+Ce, again not surprising based on relatively low weight gain. Of note is the fact that CeO<sub>2</sub> was not detected on the



**FIGURE 4.** Effect of the Ce Surface Treatment on the Oxidation Behavior of Type-430





**FIGURE 5.** The Effect of Temperature on the Oxidation Behavior of Low-Si Alloy 430-A

surface of this sample. In any event, SEM analysis is required to confirm scale formation.

**TABLE 1.** Oxide Phase Formation as a Function Exposure Temperature as Determined by XRD

	Alloy 430-A	Alloy 430-A + Ce
650°C-250 hrs	Fe-Cr alloy (major) Fe <sub>2</sub> O <sub>3</sub> (trace)	Fe <sub>2</sub> O <sub>3</sub> (major) Fe-Cr alloy trace
800°C-500 hrs	Cr <sub>2</sub> O <sub>3</sub> Mn <sub>1.5</sub> Cr <sub>1.5</sub> O <sub>4</sub>	Cr <sub>2</sub> O <sub>3</sub> Mn <sub>1.5</sub> Cr <sub>1.5</sub> O <sub>4</sub> CeO <sub>2</sub>
950°C-200 hrs	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub> Mn <sub>1.5</sub> Cr <sub>1.5</sub> O <sub>4</sub> CeO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub>

**Task 2** – Melt and fabricate 430ss-related alloys with low Si and Al.

**Progress** – A number of 430ss-related alloys with low Si and Al have been developed, fabricated, rolled and samples supplied to various groups for testing (including scientists in Tasks 1 and 3). The samples were formulated to study the effects of varying such quantities as C or Ti. Table 2 gives the composition of the alloys as fabricated as well as the 430 baseline.

Alloys NETL-430-a-c were designed as a low Si, low Al alloy with varying amounts of carbon in order to be able to investigate the effects of the variability of carbon in commercially available 430 stainless steel; NETL-430-d was designed with moderate amounts of carbon and addition of titanium for investigations of the effects of a de-oxidizer other than Si and Al with results presented

in Task 1; NETL-430-e-g was designed with a minimal level of carbon and varying the silicon to investigate a tolerable silicon level for commercially produced alloys that will meet the service requirements within the fuel cell environment. That is, if the majority of the material utilized for producing the modified 430 is from scrap, then it will necessarily contain Si and Al. Methodologies of removing the Si and/or Al during the melting of cheap, low grade scrap have been postulated. If these prove acceptable, then a production question is at what levels do the Si and Al have to be before the alloy produced becomes unacceptable? This question is being addressed by the NETL-430-e-g series in combination with Task 1. All experimental alloys have been made available to any interested parties who wish to evaluate the materials for their specific SOFC environment or application.

**TABLE 2.** NETL-430 Stainless Steel Compositions

	Al	Cr	Mn	Ti	C	Si	Fe
Commercial 430	--	17	1.00	--	0.12	1.00	Bal.
NETL-430-a	0.011	16.85	0.44	n.d.	0.0054	n.d.	Bal.
NETL-430-b	0.011	17.03	0.47	n.d.	0.0482	n.d.	Bal.
NETL-430-c	0.011	17.13	0.49	n.d.	0.1180	n.d.	Bal.
NETL-430-d	0.010	17.11	0.52	0.080	0.0123	n.d.	Bal.
NETL-430-e	0.009	16.98	0.38	n.d.	0.0045	n.d.	Bal.
NETL-430-f	0.011	17.02	0.40	0.018	0.0014	0.024	Bal.
NETL-430-g	0.010	17.28	0.45	n.d.	0.0013	0.057	Bal.

**Task 3** – Evaluate the effect of syngas on 430-related alloys with low Si and Al.

**Progress** – The NETL-430 stainless steel samples have been received as per Task 2. These samples have been prepared and are ready for exposure in the single and dual environments identified for testing. A new sample preparation and polishing procedure was developed due to the fact that traditional polishing methodologies have the potential for introducing silicon or aluminum in low amounts to the sample. Because NETL alloys have little or no Si or Al, it was deemed necessary to find a new way of preparing the samples.

The following chemical composition of the coal syngas without H<sub>2</sub>S has been selected for the corrosion experiments: 46.6% CO + 38.5% H<sub>2</sub> + 12.7% CO<sub>2</sub> + 0.01% H<sub>2</sub>O + 0.1% CH<sub>4</sub> + 1.1% Ar + 0.89% N<sub>2</sub>. This environment was based upon publications on the syngas compositions from various gasification processes and through private consultations with gasifier manufacturers. Meanwhile, late in FY 2006, the furnace utilized in the dual environment testing failed. A new furnace has been purchased and installation is

proceeding with an expected completion date of March 31, 2007. At this time, a series of dual environment tests will be conducted on the NETL alloys.

Corrosion experiments on NETL low Si low Al 430-A, NETL-430-1, 430 – commercial, Crofer 22APU, NETL J5, J1, Haynes 230, and Haynes 242, in a single environment of 45 vol% CO+12 vol% CO<sub>2</sub>+0.01 vol% H<sub>2</sub>O+4.19 vol% N<sub>2</sub> at 800°C was initiated.

Oxidation kinetics of Crofer 22APU in simulated air at 800 °C using thermogravimetric analysis (TGA) is being determined.

## Conclusions and Future Directions

### Task 1 – NETL-430 Stainless Steel Compositions

Determine the mechanisms used in surface infusion treatments, including CeOx, for improved oxidation resistance.

The mechanism of improved oxidation resistance by surface treating candidate materials for interconnects and other balance-of-plant applications has been studied. The mechanism was determined to be the preferential pre-oxidation of the surface to form a Ce-modified oxide. The incorporation of the rare earth metal in turn slows the scale growth, and thus, enhances oxidation resistance through the well known reactive (rare) element effect. The NETL-430 family of alloys (Task 2) were tested with and without the CeOx treatment with interesting results. Briefly, the CeOx treatment enhances the oxidation resistance at the operating temperature of the fuel cells. Interestingly, though, this does not appear to be as prevalent at lower temperatures. Crofer 22APU was also tested, both as a baseline for the 430 family of alloys and for comparison with other rare earth treatments, specifically lanthanum. The lanthanum treatment shows similar characteristics with respect to oxidation resistance that the cerium treatment has. It is expected that the ASR of the La treated samples will be decreased slightly in comparison to the Ce treated samples due to the overall cleaner state that the La treatment gives. The mechanism of oxidation resistance by rare earth surface infusion, specifically cerium, will be published in peer reviewed journals during the second half of this year. Meanwhile, once an invention disclosure is complete, the lanthanum treatment will be published as well. Future work will include measuring the ASR of lanthanum treated steels at SOFC operational temperatures and comparing behavior to cerium treated steels and untreated steels.

**Task 2 – Melt and fabricate 430ss-related alloys with low Si and Al.**

One result from the controlled, low Si 430 melts is that they end up with about half of the designed amount

of Si. The melts were poured with little superheat (about at the liquidus temperature) so there was a heavy skull left in the crucible. The thermodynamic analysis (ThermoCalc) suggests that the liquid was enriched with Si at this temp rather than the first solid to form at that temperature; interestingly, this is opposite of the results and may require further investigations.

A second way to reduce the Si in commercial 430, which, for cost purposes, will be made with recycled material (which includes high amounts of Si) would be to utilize a slagging process which scavenges the Si from the molten metal. Initial studies and “back of the envelope” calculations indicate that this can be done if it is determined that NETL should pursue this topic further.

**Task 3 – Evaluate the effect of syngas on 430-related alloys with low Si and Al.**

This task is ongoing. Single environment testing for oxidation (cathode side) has been completed (Task 1) while single environment testing on the anode side is underway. Preliminary results will be available shortly with long term results at the end of the fiscal year.

## FY 2007 Publications/Presentations

### Publications

1. D.E. Alman, C.D. Johnson, W.K. Collins and P.D. Jablonski, “The Effect of Cerium Surface Treated Ferritic Stainless Steel Current Collectors on the Performance of Solid Oxide Fuel Cells (SOFC), accepted for publication in J. Power Sources, 2007 (in press).
2. M. Ziomek-Moroz, T.A. Adler, K-S. Kwong, G.R. Holcomb, L. Penner, “Corrosion performance of metallic materials in carbon oxide – containing atmosphere for solid oxide fuel applications,” submitted to the 32<sup>nd</sup> International Technical Conference on Coal Utilization and Fuel Systems, Session: Coal Compatible Fuel Cells.
3. M. Ziomek-Moroz, B.S. Covino, G.R. Holcomb, S.J. Bullard, “Chemical Stability of Ferritic Steel in Carbon-containing Atmosphere for SOFC Applications,” Proceedings of the Materials Science & Technology 2006 Conference and Exhibition, Cincinnati, OH, October 15-19, 2006.
4. M. Ziomek-Moroz, T. Adler, P. King, “Materials Performance of Ferritic Steel in Combustion Gases for Heat Exchanger Applications in Solid Oxide Fuel Cell Systems” M. Ziomek-Moroz, T. Adler, P. King to appear in proceedings, CORROSION 2008.
5. M. Ziomek-Moroz, T. Adler, D. E. Alman, P.D. Jablonski, J. Clark, L.R. Penner, “Materials Performance of Modified 430 Stainless Steel in Simulated SOFC Stack Environments for Integrated Gasification Fuel Cell System Applications” to appear in proceedings of the Fuel Cell Seminar, 2007.

## Presentations

1. M. Ziomek-Moroz, B.S Covino, G.R. Holcomb, S.J Bullard, "Chemical Stability of Ferritic Steel in Carbon-containing Atmosphere for SOFC Applications," presented at Materials Science & Technology 2006 Conference and Exhibition, Cincinnati, OH, October 15-19, 2006.
2. D.E. Alman and P.D. Jablonski, "Influence of a Ce-Surface Treatment on the Oxidation Behavior of Commercial Fe- and Ni- Based Alloys" at MST'2006 Symposium on High Temperature Degradation of Fe-, Ni-, and Co- Based Alloys Including Metal Dusting: Alloying Elements and Corrosive Environments, October 15-19, 2006.
3. P.D. Jablonski and D.E. Alman, "Evaluation of Experimental Ni-Base and Fe-Base Alloys Containing Lower Chrome," at MST'2006 Symposium on Fuel Cells and Energy Storage Systems: Materials, Processing Manufacturing and Power Management Technologies: Interconnection and Metallic Materials in SOFCs, October 15-19, 2006, Cincinnati, OH.
4. G.R. Holcomb and D.E. Alman, "Oxidation of Interconnect Alloys in an Electric Field," at MST'2006 on Symposium Fuel Cells and Energy Storage Systems: Materials, Processing Manufacturing and Power Management Technologies: Interconnection and Metallic Materials in SOFCs, October 15-19, 2006, Cincinnati, OH.
5. D.E. Alman, C.D. Johnson, and P.D. Jablonski, "Evaluation of a Surface Treatment on the Performance of Crofer 22APU," at TMS-2007, Symposium on Materials in Clean Power Systems II, Solar and Hydrogen Based Technologies: SOFC," February 25 – March 1, 2007, Orlando, FL.

## Invited Talks

1. P.D. Jablonski and, D.E. Alman "Evaluation of Model 6-22 Cr Ferritic Alloys For Interconnect Applications," at TMS-2007, Symposium on Materials in Clean Power Systems II, Solar and Hydrogen Based Technologies: SOFC," February 25- March 1, 2007, Orlando, FL.
2. R.D. Wilson, O.N. Dogan, P. King, "Welding of Dissimilar Alloys for High Temperature Heat Exchangers for SOFC," Materials Science and Technology 2006, Cincinnati, OH, October 15-19, 2006.
3. M. Ziomek-Moroz, T. Adler, P. King, "Materials Performance of Ferritic Steel in Combustion Gases for Heat Exchanger Applications in Solid Oxide Fuel Cell Systems" M. Ziomek-Moroz, T. Adler, P. King to appear in proceedings, CORROSION 2008.
4. M. Ziomek-Moroz, T. Adler, D. E. Alman, P.D. Jablonski, J. Clark, L.R Penner, "Materials Performance of Modified 430 Stainless Steel in Simulated SOFC Stack Environments for Integrated Gasification Fuel Cell System Applications" to appear in proceedings of the Fuel Cell Seminar, 2007.

## References

1. D.A Downham and S.B. Shendye, Oxidation of Metals, Vol. 43, Nos5/6, 1995, p. 411.
2. S. Chevalier et al, Surf. Coat. Tech., Vol. 100–101, 1998, p. 208.
3. D.E. Alman, P. D. Jablonski and S. C. Kung, in Ceram. Engr. Sci. Proc., Vol. 27, Issue 4, ed N.Bansal, Amer. Ceram. Soc., Westerville, OH, 2006. p. 253.